

CLAIMS

1. Process for manufacturing an electrochemical device including a cathode, an anode and at least one electrolyte membrane disposed between said anode and said cathode, wherein at least one of the cathode, the anode and the electrolyte membrane, each containing at least a ceramic material, is produced by performing at least the following steps of:

10 - thermally treating an aqueous solution comprising at least one metal cation, at least one hydrosoluble ethylenically unsaturated monomer with an ester moiety, and a hydrosoluble cross-linking monomer with at least two ethylenically unsaturated ester moieties, to provide a gel and to obtain said at least one metal cation in an oxide form;

15 - calcining said gel to remove organic substances and to form a crystal phase of said at least one metal oxide in a nanosize powder form;

20 - sintering said powder to provide the ceramic material.

2. Process according to claim 1 wherein the electrochemical device is a solid oxide fuel cell.

3. Process according to claim 1 wherein the anode contains a material selected from

25 - a cermet material comprising a metallic portion selected from copper, aluminum, gold, praseodymium, ytterbium, cerium, nickel, iron, cobalt, molybdenum, platinum, iridium, ruthenium, rhodium, silver, palladium, and a ceramic portion selected from yttria-stabilized zirconia, ceria doped with gadolinia or samaria, and $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ wherein x and y range from 0 to 0.7, extremes included, and δ is from stoichiometry; and

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- a ceramic material selected from cerium oxide, manganese oxide, molybdenum oxide, titania, ceria doped with gadolinia or samaria, niobia-doped ceria, and perovskites.

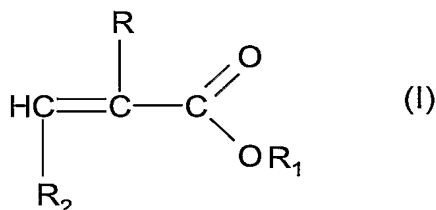
- 5 4. Process according to claim 1 wherein the electrolyte membrane contains a ceramic material selected from yttria-stabilized zirconia, ceria doped with gadolinia or samaria, and $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ wherein x and y range from 0 to 0.7, extremes included, and δ is from stoichiometry.
- 10 5. Process according to claim 1 wherein the cathode contains a material selected from oxides of rare earth elements, perovskites optionally in combination with a doped ceria, and mixtures thereof.
6. Process according to claim 1 wherein the aqueous
15 solution comprises water or water with at least one hydrosoluble solvent.
7. Process according to claim 6 wherein the hydrosoluble solvent is selected from an alcohol, glycol, tetrahydrofuran, dioxane.
- 20 8. Process according to claim 1 wherein the at least one metal cation is selected from lanthanum, strontium, chromium, zirconium, yttrium, aluminium, lithium, antimony, boron, cadmium, cerium, cobalt, copper, dysprosium, erbium, europium, gallium, gold, hafnium, holmium, iridium, iron,
25 lutetium, manganese, molybdenum, nickel, niobium, osmium, palladium, platinum, praseodymium, rhenium, rhodium, rubidium, ruthenium, samarium, scandium, silver, sodium, tantalum, terbium, thorium, thulium, tin, titanium, tungsten, uranium, vanadium, ytterbium cations.
- 30 9. Process according to claim 1 wherein the at least one metal cation solution is obtained by dissolving a hydrosoluble precursor selected from oxides, chlorides, carbonates, β -diketonates, hydroxides, nitrates, acetates,

oxalates, and mixtures thereof.

10. Process according to claim 1 wherein, in the aqueous solution, the at least one metal cation is in a concentration higher than 0.5 mol/l.

5 11. Process according to claim 10 wherein, in the aqueous solution, the at least one metal cation is in a concentration from 1 to 10 mol/l.

12. Process according to claim 1 wherein the hydrosoluble ethylenically unsaturated monomer has general formula (I)



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wherein R is hydrogen, (C₁-C₄)alkyl, aryl or aryl(C₁-C₄)alkyl; R₁ is a C₁-C₈ hydrocarbon group containing at least one polar group selected from -COOH, -NH₂, -NHR', -N(R')₂, -OH, -OR', -SO₃H, -SH, wherein R' is a (C₁-C₆)alkyl group; and R₂ is hydrogen, methyl, ethyl, propyl or phenyl.

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13. Process according to claim 12 wherein R' is a (C₁-C₄)alkyl group.

14. Process according to claim 12 wherein the ethylenically unsaturated monomer is selected from 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl phenacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, butandiol monoacrylate, 2-(2-ethoxyethoxy)ethyl acrylate, dimethylamino ethyl acrylate, and dimethylamino ethyl methacrylate.

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15. Process according to claim 1 wherein the cross-linking monomer is selected from diacrylates and triacrylates wherein the acrylates groups are linked to alkoxyated

moieties or polyoxialkylene linear units.

16. Process according to claim 15 wherein the cross-linking monomer is polyethyleneglycol diacrylate or ethoxylated tromethylolpropanetriacrylate.

5 17. Process according to claim 1 wherein the aqueous solution comprises a hydrosoluble polymerization initiator.

18. Process according to claim 17 wherein the hydrosoluble polymerization initiator is α,α' -azaisobutyronitrile (AIBN), tetramethylene-ethylenediamine, hydrogen peroxide,
10 benzoyl peroxide, dicumyl peroxide, ammonium, sodium or potassium persulfate,.

19. Process according to claim 1 wherein the thermal treatment is effected at a temperature ranging between 50°C and 150°C.

15 20. Process according to claim 1 wherein before proceeding to the calcining step, the gel is dried to obtain a xerogel.

21. Process according to claim 20, wherein the gel is dried at a temperature ranging between 80°C and 300°C.

20 22. Process according to claim 20 wherein the xerogel is disaggregated and subjected to the calcining step.

23. Process according to claim 1 wherein the calcining step is carried out at a temperature ranging between about 300°C and about 1500°C.

25 24. Process according to claim 1 wherein the calcining step is carried out by progressively increasing temperature.

25. Process according to claim 1 wherein at least one grinding step of the powder is carried out at an intermediate stage of the calcining step.

30 26. Process according to claim 1 wherein the nanosize

powder show a mean primary grain size lower than 20 nm.

27. Process according to claim 26 wherein the nanosize powder show a mean primary grain size comprised between 3 nm and 15 nm.

5 28. Process according to claim 1 wherein a reduction step is effected together with the sintering step.

29. Process according to claim 28 wherein the reduction step is effected under hydrogen atmosphere.

10 30. Process according to claim 1 wherein the sintering of the nanosize powder is preceded by a shaping step to shape the nanosize powder in form of anode, cathode or electrolyte membrane for electrochemical devices.

31. Process for manufacturing a nanosize oxide powder, the process comprising the steps of:

15 - thermally treating an aqueous solution comprising at least one metal cation, at least one hydrosoluble ethylenically unsaturated monomer with an ester moiety, and a hydrosoluble cross-linking monomer with at least two ethylenically unsaturated ester moieties, to
20 provide a gel and to obtain said at least one metal cation in an oxide form;

 - calcining said gel to remove organic substances and to form to form a crystal phase of said at least one metal oxide in nanosize powder form.